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INTEROFFICE CORRESPONDENCE

DATE: November 2, 1990 MIL-5-90 4 D/02

TO: E. B. Wilson, Remedial Programs, T130B

FROM: M. I. Litaor, EMAD Bldg. T130B, X5970 Iggy Litaor

SUBJECT: COMMENTS ON ENVIRONMENTAL RESTORATION PROGRAM FOR OPERABLE UNIT NUMBER 2

I would like to suggest several changes and modifications to the **surficial soil program** proposed in the final draft of PHASE II RFI/RIFS WORK PLAN.

During the last 6 weeks I have conducted a thorough evaluation of published and unpublished reports regarding Soil-Pu in soils around Rocky Flats plant (RFP). Most of my suggestions stem from this review which included appraisal of the spatial distribution of Soil-Pu east of the 903 Pad using geostatistcal techniques. It is clear that the authors of the Work Plan for Operable Unit NO. 2 were not that familiar with the enormous wealth of data accumulated since the first remedial action regarding the 903 Pad was implemented back in 1971.

Statement of the Problem

Phase I RI concluded that surficial soils in the area east of 903 Pad are contaminated with Pu, Am, and other radionuclides (such as ???) due to wind dispersal of soil particles during cleanup operations. Soil sampling results indicated that the actinides are most enriched near the surface, but further investigation of smaller soil intervals is necessary to assess the distribution of these radionuclides.

Objectives

The work plan in the Final Phase II RCRA Facility Investigation (Operable Unit NO. 2) suggests: (1) Analytical data from surficial soil scraps and vertical soil profiles will be evaluated in order to characterize the areal and vertical distribution of Pu and Am contamination in remedial investigation areas and in the buffer zone, and (2) The possibility of using kriging to contour the isopleths of the most widely distributed contaminants will be investigated.

Historical Review

The need for better understanding of the physicochemical characteristics of Pu were recognized many years ago by the Committee Evaluation of Pu Levels in Soils within and surrounding USAEC Installation at Rocky Flats, Colorado (Seed et al., 1971). They recommended that the mechanism of Pu transport in soil will be addressed, and the chemical form of Pu in RFP soils should be determined.

In response to these recommendations an intensive and extensive studies were conducted. The intensive study site is located approximately 1.5 km east of 903 Pad (Site 16, Fig. 1). Soil samples were collected between 1979 and 1983 to assess the vertical and the horizontal

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distribution of Pu in RF soils (RFP-ENV-84). Composite samples were collected from 60- $2m^2$ plots which were 1 m apart. Samples were taken from 0-5 cm and 5-20 cm intervals. The mean and the standard deviation of Soil-Pu concentrations in the surface and the subsurface horizons were 10.2 ± 2.7 and 1.1 ± 0.4 respectively. The vertical profile of the data distribution suggests that some Soil-Pu has migrated down the soil column. However, there is little information or understanding of the actual mechanism of Pu transport within the soils of Rocky Flats plant. **The proposed work plan does not address this important issue.**

The spatial variations in Soil-Pu concentrations in site 16 are illustrated in Figures 2 and 3. There is no clear spatial trend in the concentrations of Soil-Pu in both depths. Indeed, analysis of the spatial variations of Soil-Pu within this site failed to produce a meaningful variogram (Fig. 4; Variogram measures the degree of correlation among sample values in a given area as a function of the distance and direction between samples. These values are later can be used for estimation of kriging weights). The results of the variogram suggest that the Soil-Pu values are spatially independent from each other or were randomly distributed. In reality, the grid size was too small for a meaningful evaluation of the spatial pattern of Soil-Pu in soils around RFP.

The extensive study sites are located east of the 903 Pad (Figs 1 & 5). The concentrations of Soil-Pu depicted in Fig. 5 clearly suggest a spatial trend from west to east. The variogram computation suggests a linear model with no sill or range and a nugget (systematic change over distance) of 0.75 (Fig. 6). The most commonly used variogram models in geochemical application are the spherical and exponential models. These models imply that there is a measurable distance or barrier that controls the spatial distribution of a given element. The findings that the concentrations of Soil-Pu in surface soils east of RF are best described by linear model with no actual limit on spatial dependency suggest that wind is the most probable force that control Pu transport across the landscape. Kriging estimates using the linear model were computed for the extensive study sites and are depicted in Figures 7, and 8. Figure 7 depicted contours of Soil-Pu concentrations in the buffer zone east of 903 Pad. Figure 8 illustrated the kriging standard of error estimates which are low in the west-east direction, which verified the goodness-of-fit of the kriging estimates in this direction.
The highest estimate of Soil-Pu concentration was found 500-600 meters east of 903 Pad which may resulted from storage practices of radioactive waste in the east trenches area. **More soil samples around the east trenches area are needed to verify this hypothesis.**

Source of Variations in Soil-Pu Concentrations in Surface Soils
In constructing these spatial distribution estimates I have excluded the area immediately adjacent to the 903 Pad because of extremely large variations in Soil-Pu (Table 1). Similar problem was reported by Delfiner and Gilbert (1978) who found chaotic distribution of Soil-Pu near ground zero at Nevada test site. Concentrations of Pu in soils especially near the source are highly variable, with coefficients of variation usually exceeding 1.0 (Pinder and Paine, 1980). A portion of this large variation is due to the release of Pu in particulate form and the analytical error caused by including various amounts of these particles in the sample (Doctor et al., 1980).

Pinder and Paine (1980) ascribed the variations in ^{239,240}Pu to distance from point of release (75%), microtopographical variations (20%) and sampling error, which included subsampling and analytical error (5%). Little et al. (1980) speculated that the large range in Pu concentrations may derived from many small Pu particles agglomerated with large soil particles to form aggregates. The proposed work plan suggests to use the CDH protocol which requires 25 E. subsamples within 10-acre area to be composited to one soil sample. **In light of the above review it is clear that smaller parcel of land (< 5-acre) should be used to increase the number of soils analyzed immediately adjacent to 903 Pad and around East Trenches area.**

Table 1. Soil-Pu concentrations in surface soils east of 903 Pad

	pCi/g		
	X	S.D.	Range
Campbell (1984)	1024	978	74 - 3700 (RFP)
Folger (unpublished,	267	173	2 - 566 (RFP)
samples taken	147	90	8 - 283 (CDH)
in 1990)			

The use of kriging techniques was explicitly stated as a tool for evaluation of spatial distribution of pollutants in soils. The proposed Work Plan suggests 57 surface soils to be sampled and analyzed. This limited number of soils is hardly sufficient for construction of a valid variogram. Hence, the more intensive sampling design immediately east of 903 Pad and around East Trenches area will serve dual functions: (1) increased our confidence in Soil-Pu estimates around 903 Pad and East Trenches area and (2) expanded the number of soil data for kriging purposes.

Physicochemical Association of Pu in RF Soils

Static Soil Phase

The Work Plan suggests to sample 24 soil profiles to assess vertical distribution of ^{239,240}Pu in soils east of RF plant. Little additional information will be gained by this study if analyses are restricted to Pu determination only!

The contamination of soils around Rocky Flats (RF) plant by Pu oxides was mainly caused by leaking barrels of Pu-contaminated oil (Krey and Hardy, 1971). Plutonium in oxidation state (IV) is very insoluble in water in the absence of soluble complexes (Bondietti and Tamura, 1980). Bondietti et al. (1976) removed 82% of the soil-Pu by repeated bleaching experiment with NaOCl at pH 9.5 which minimized inorganic mineral destruction. This removal suggests that large portion of soil-Pu is associated with organic C and that Pu is associated with the soil via surface-sorbed mechanisms. Moreover, they found that Pu is not bound by cation exchange reactions in the soil. The release of organic chelates agents is strongly depend on pH and E. B.

decalcification processes within the soil (Bondietti and Tamura, 1980). Hence, in order to better understand the mechanisms of vertical transport of Pu in soils a sequential extraction of soil matter from 3-5 soil profiles east of 903 Pad should be conducted. Plutonium determination will be performed on each of the sequential extract to assess the physicochemical association of Pu with organic C, $CaCO_3$, and sesquioxides. The organic C will be extracted by NaOCl at pH 9.5, $CaCO_3$ will be removed by 0.5 M sodium acetate ($NaC_2H_3O_2 \cdot H_2O$), adjusted to pH 5, and the sesquioxides will be extracted by citrate-bicarbonate-dithionite buffer (Kunze and Dixon, 1986). In addition, the following analyses should be conducted on all samples from the 24 soil profiles: (1) soil organic C, (2) soil pH, (3) $CaCO_3$ content, (4) sesquioxides contents, and (5) specific conductance. The specific conductance will be used to calculate the ionic strength of the soil slurry (Lindsay, 1979).

Mobil Soil Phase

The Work Plan asserted that there is considerable interaction between surface water and ground water. As a result, organic contamination is observed in seeps downgradient of the 903 Pad and the upper reaches of South Walnut Creek at the Mound area. Plutonium mobility down the soil column is probably controlled by the abundance and mobility of organic chelates and physical processes such as frost heave cycles and swelling and shrinking of clay within the soil. The movement of organic chelates and soil particles are govern by the physical characteristics of soil interstitial waters. The excavation of 24 soil pits will allow us to install various soil solution samplers to measure and characterize the movement of water, solute and radionuclides down the soil column. Attached is a mini-proposal to study soil interstitial waters in conjunction with the proposed Work Plan.

csk

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Figure. 1. The locations of sites for the intensive and extensive soil studies east of 903 Pad.

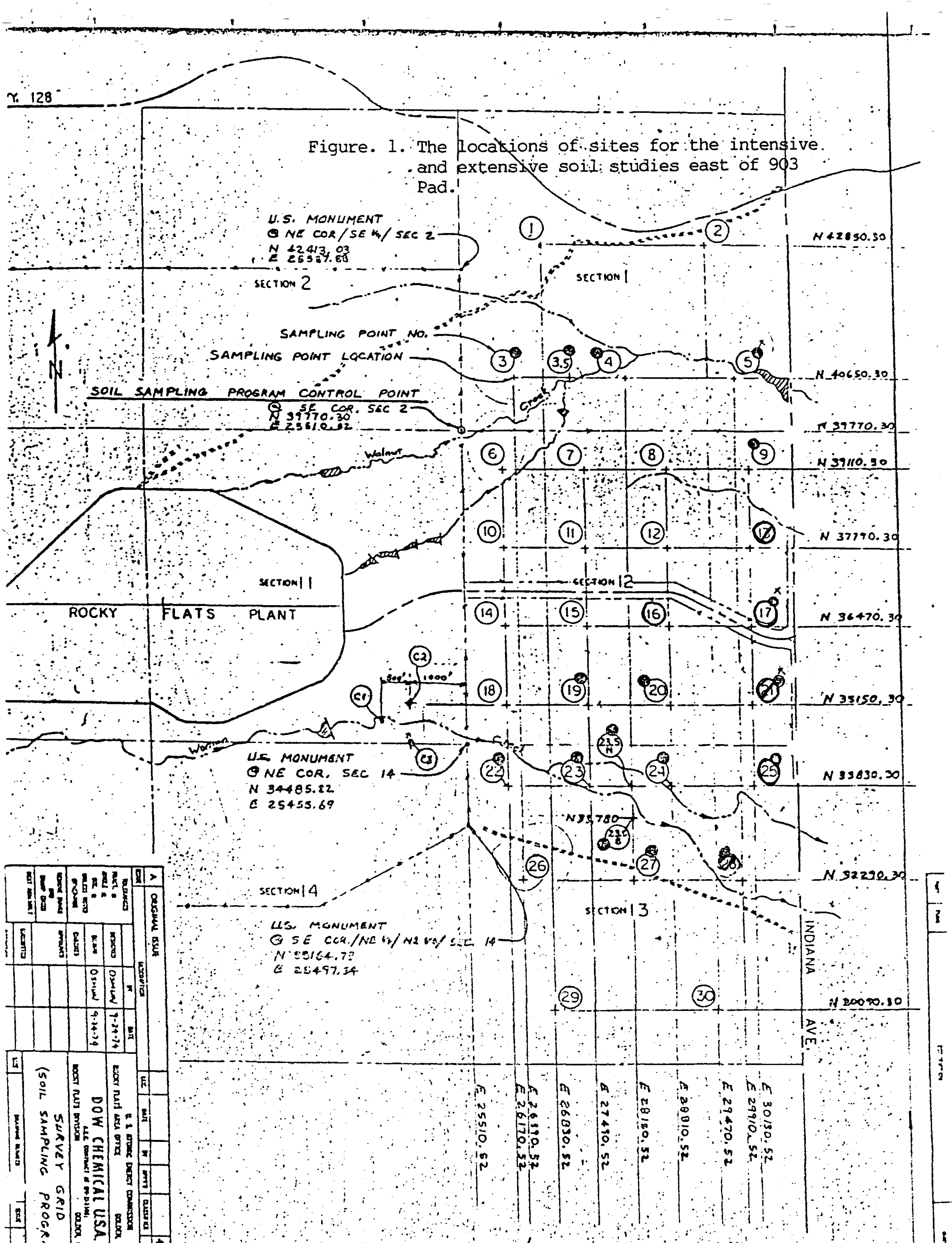


FIGURE 1

Figure 2.

Pu Concentrations in Surface Soils (0–5 cm) at Site 16

Samples collected between 1979 and 1983

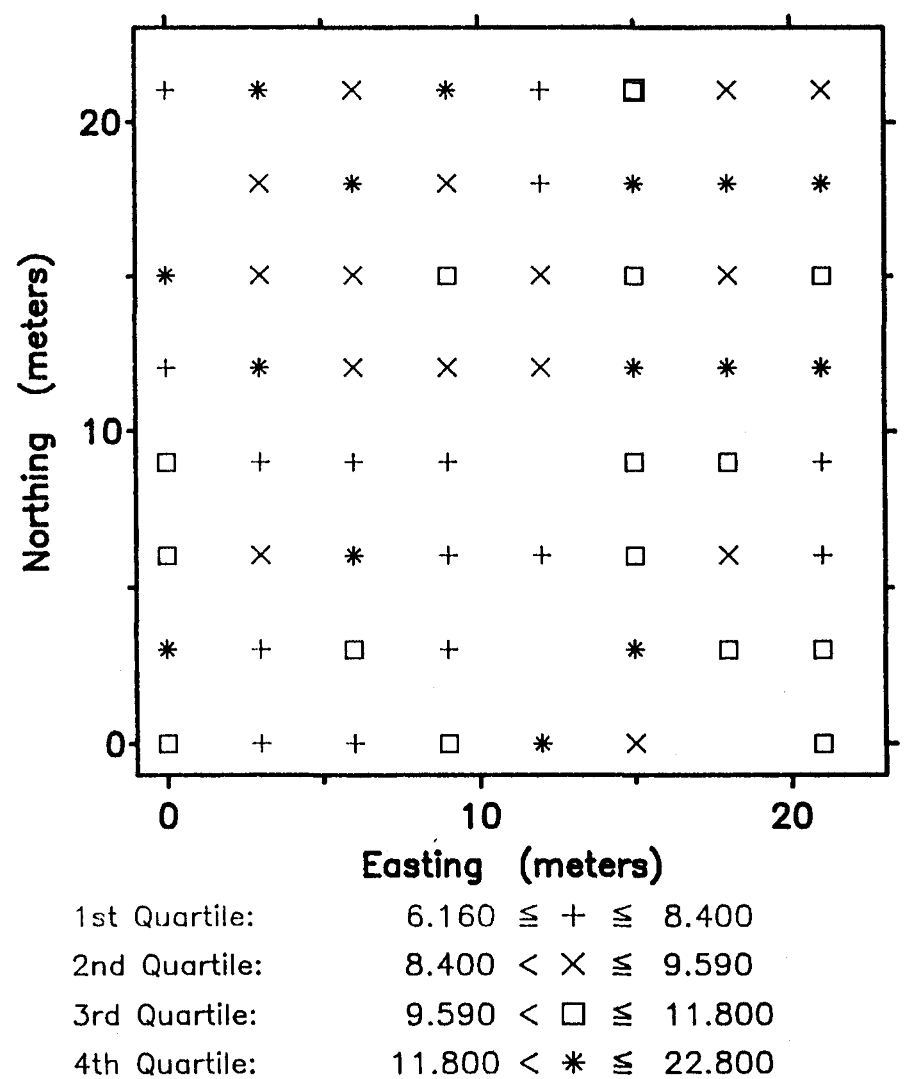
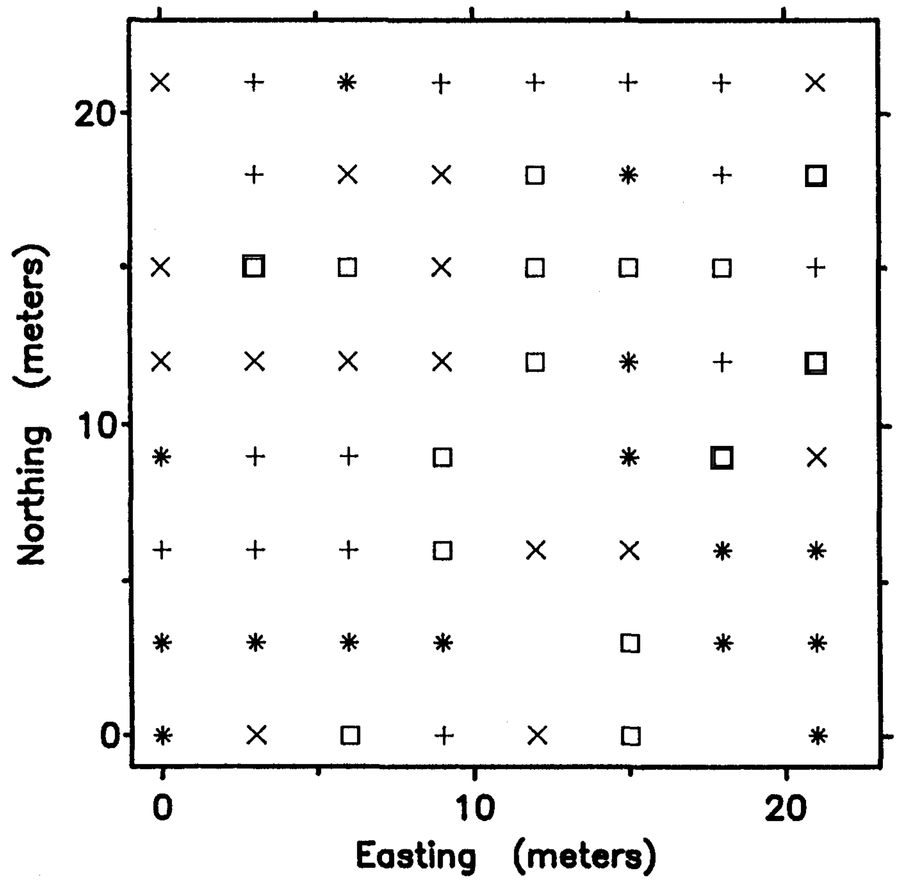


Figure 3.

Pu Concentrations in Subsurface Soils (5–25 cm) at Site 16
Samples collected between 1979 and 1983



1st Quartile: .240 ≤ + ≤ .800
2nd Quartile: .800 < × ≤ 1.010
3rd Quartile: 1.010 < □ ≤ 1.420
4th Quartile: 1.420 < ✳ ≤ 2.830

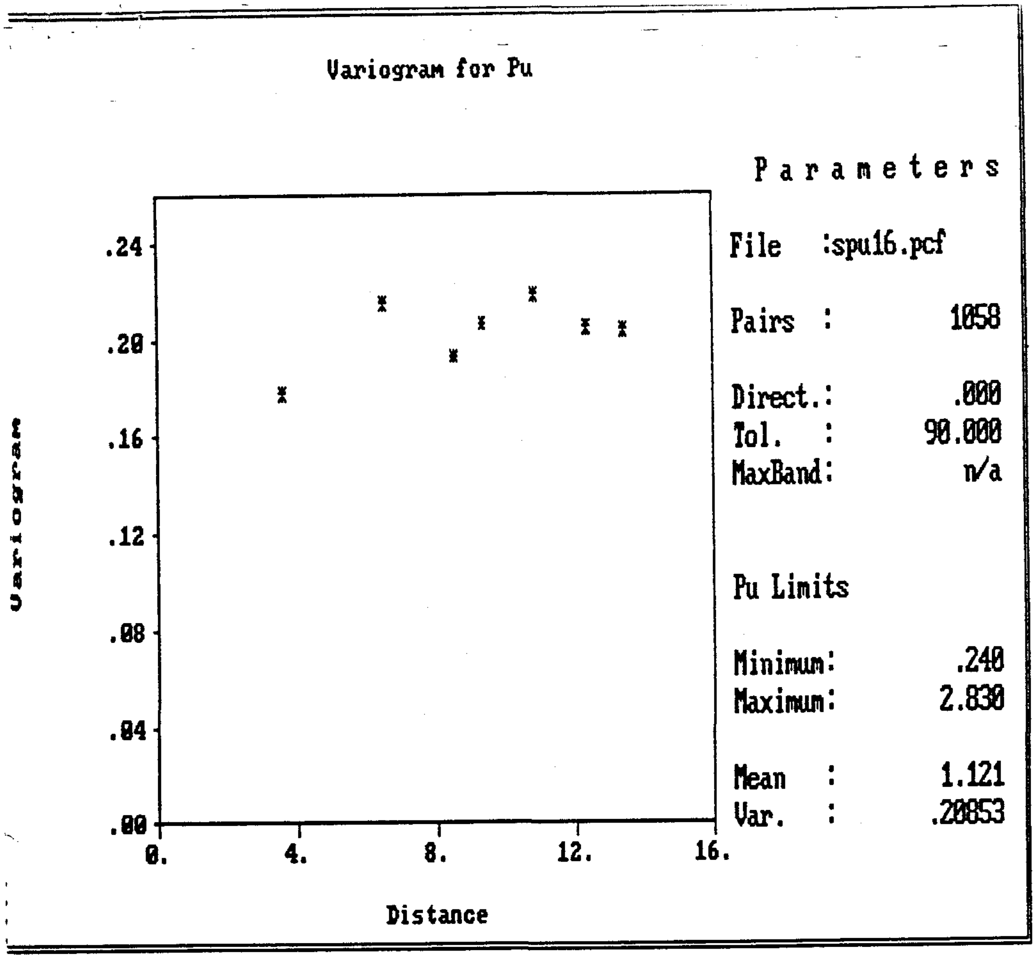
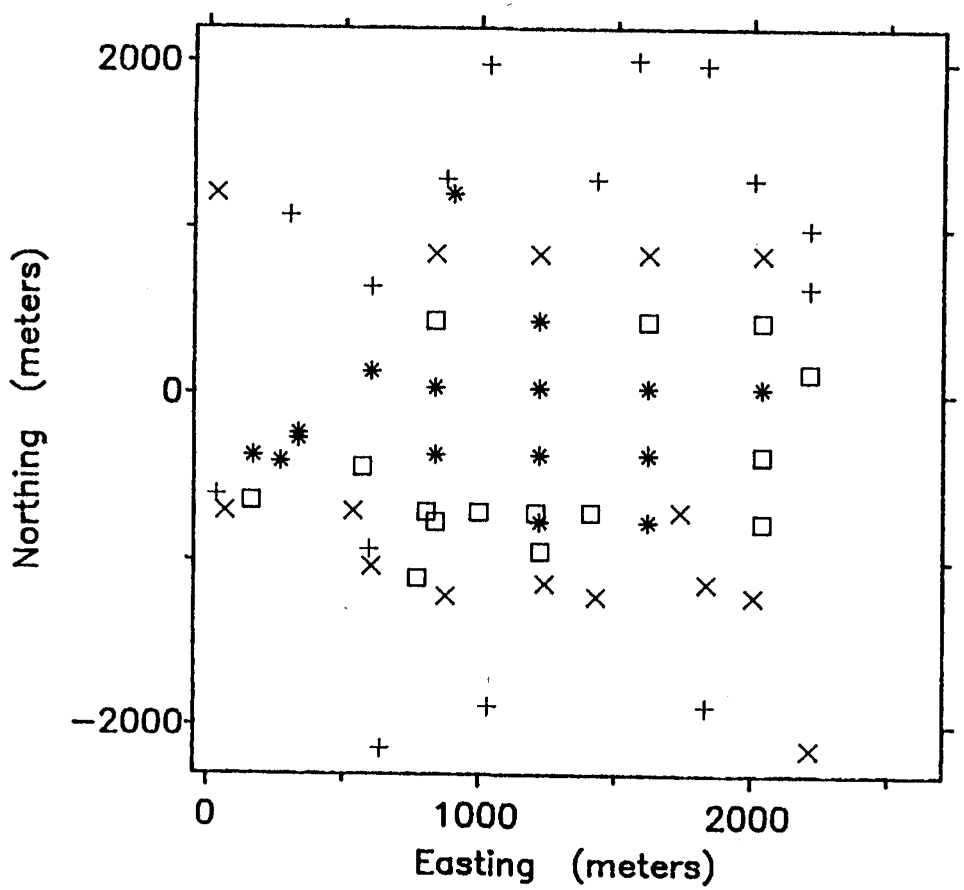


Figure 4. Variogram for Soil-Pu concentrations calculated from 60 soil samples (intensive study) in site 16.

Figure 5.

Soil–Pu concentrations East of 903 Pad

Samples collected from 1975 to 1983



1st Quartile:	.010 ≦ + ≦ .369
2nd Quartile:	.369 < × ≦ 1.395
3rd Quartile:	1.395 < □ ≦ 3.645
4th Quartile:	3.645 < ✳ ≦ 36.630

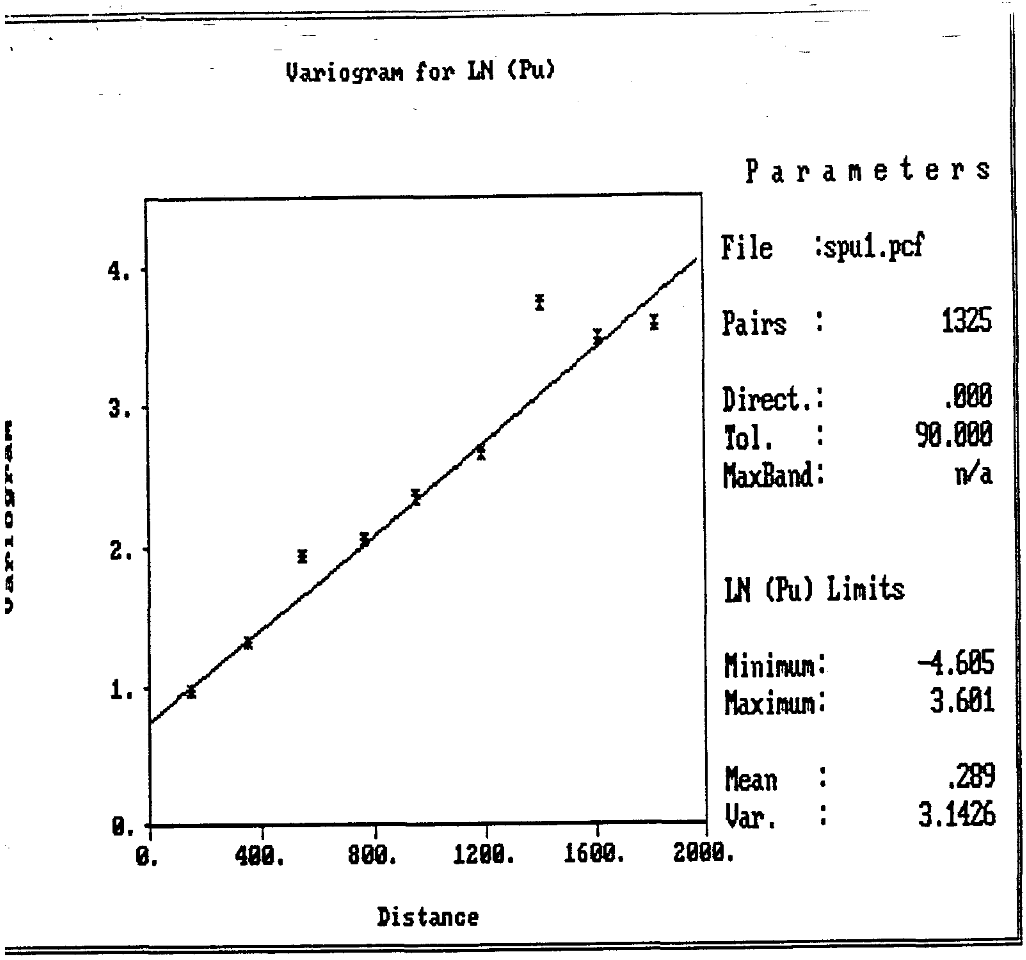
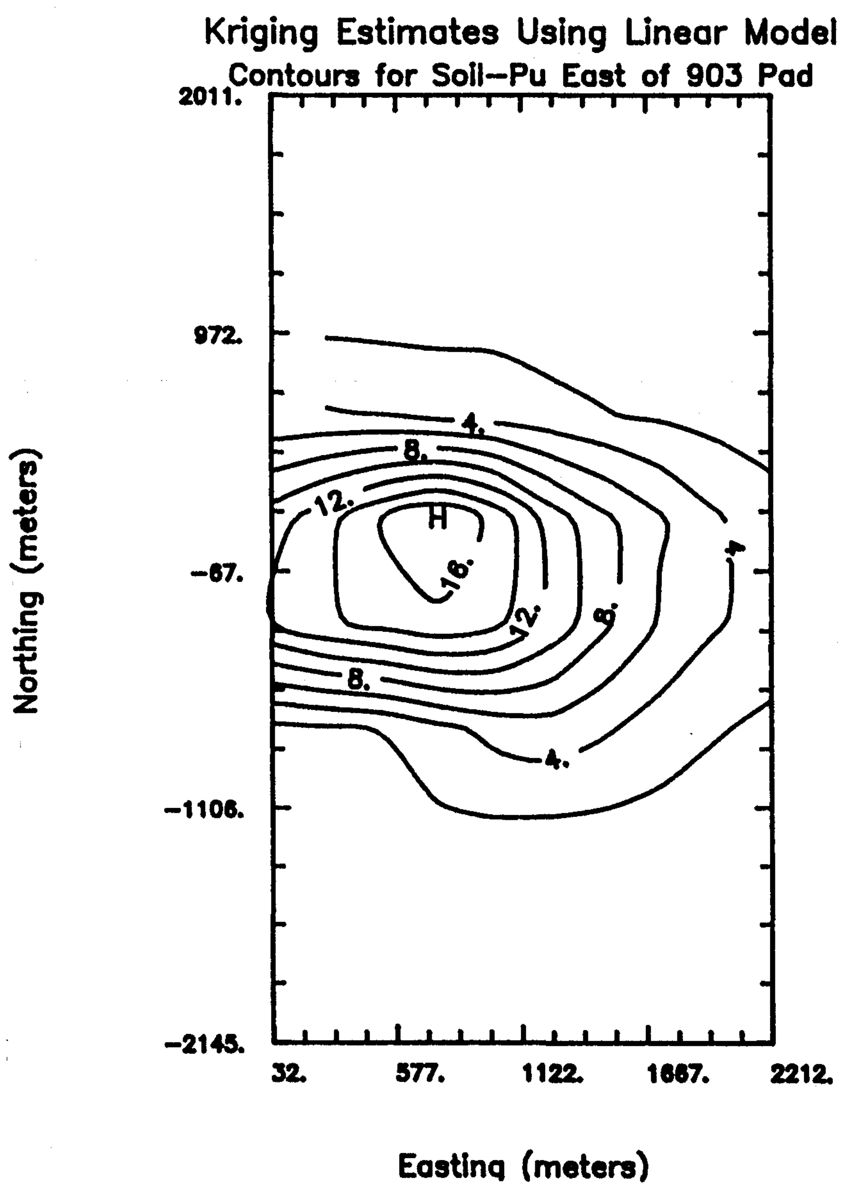


Figure 6. Variogram for Soil-Pu concentrations calculated from 68 soil samples (extensive study) east of 903 Pad.

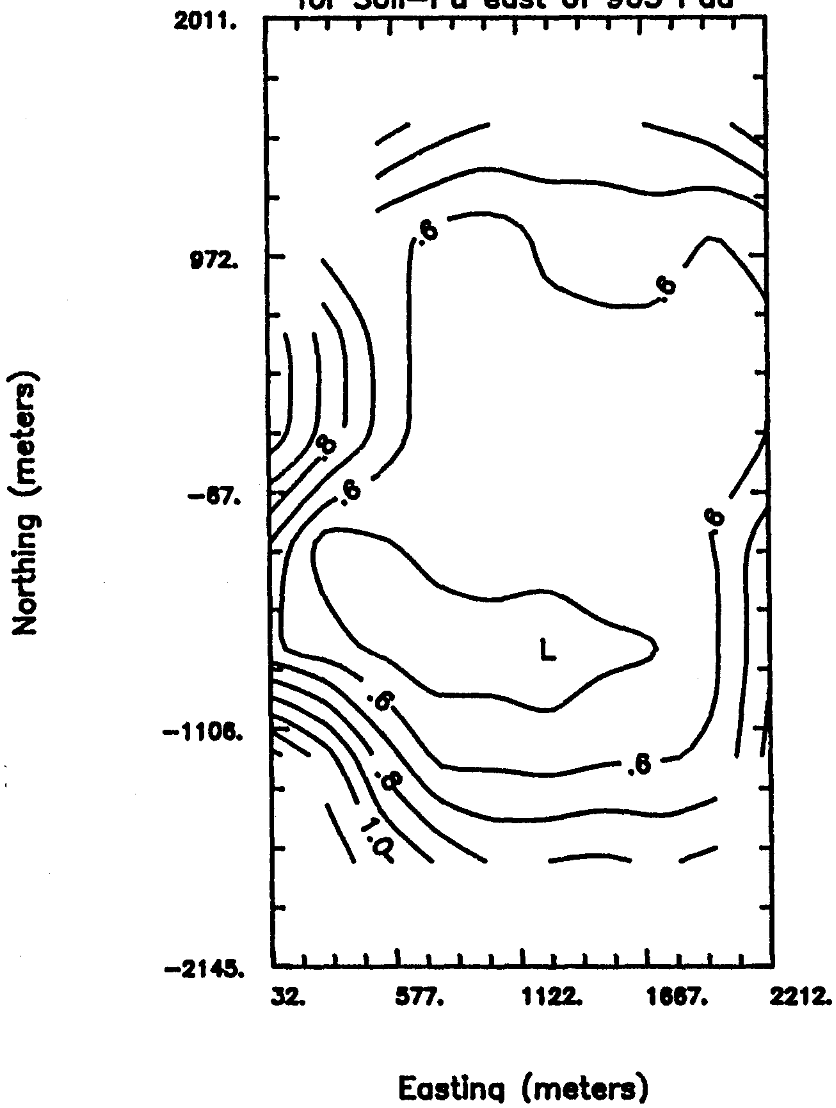
Figure 7.



Kriging Estimates Using Linear Model
Contours for Soil—Pu East of 903 Pad
2011.
972.
-67.
-1106.
-2145.
32.
577.
1122.
1667.
2212.
4.
8.
12.
16.
H
Northing (meters)
Easting (meters)

Figure 8.

Kriging Estimates Using Linear Model
Contours represent standard error of estimates
for Soil-Pu east of 903 Pad



MINI-PROPOSAL

INTRODUCTION

Reports of plutonium (Pu) and americium (Am) movement in groundwater over distances beyond several meters are rare. Hakonson et al (1981) reviewed the transport of Pu in terrestrial systems and asserted that vertical leaching of soluble Pu through the soil is a probably important phenomenon. Recently, Penrose et al (1990) found that Pu and Am were transported in groundwater for at least 3390 meters downgradient from the point of discharge. Plutonium and americium were tightly or irreversibly bound to colloidal material (25 to 450 nm).

Little research has been conducted on the transport of actinides from soils and sediments to the water table at Rocky Flats Plant. Moreover, there are no studies on the physicochemical characteristics of interstitial waters in soils and sediments from Solid Waste Management Units on plant-site. There are several areas of concern in Rocky Flats Plant from which actinides and other pollutants may leach through the soils to the ground water. These sites include 881 hillside, 903 Pad and its vicinity, the East Trenches (Operable Unit 2), and the Solar Evaporation ponds.

BACKGROUND

Environmental fate of actinides in soils are usually studied by extracting the soil matter. In general, these analyses fail to provide important information regarding the spatial and temporal distribution of pollutants, as well as their transport characteristics within the soil column. Furthermore, sampling of soil solutions in situ can provide crucial information on flow and solute transport mechanisms within the soil column.

Analysis of the frequency, duration and intensity of summer precipitation events and spring snowmelt events coupled with direct measurements of solute transport in soils using soil solution samplers will provide essential information to assess the form and magnitude of actinide movement in soil.

The proposed research design is based on 2 hypotheses: (1) leaching episodes in the soils will transport solute and colloidally bound actinides down the soil column, and (2) freely flowing waters in the soil environment will carry different actinide concentrations than soil solutions collected at higher matric potentials.

Testing these hypotheses will require in-situ sampling of soil interstitial waters through time. More specifically, it will be necessary to develop a fully automated, remotely controlled, soil solution sampling system that is capable of (a) collecting freely flowing water (0-5 kPa matric potential) mainly via macropores, (b) collecting soil solutions flowing in micropores at higher matric potential (5-40 kPa), and (c) provide an accurate and timely measurements on incoming precipitations. This apparatus will consist of two major modules: (a) an automated zero-tension sampler, in which freely flowing water mainly in macropores (formed by frost heave cycles and swelling and shrinking of clays), will be accurately and timely collected for assessing the subsurface flow during and after major precipitation events; (b) a fluxmeter which will provide the unsaturated flux as the soil dries out.

OBJECTIVES

The objectives of the proposed work are: (1) to measure vertical flow of water and solute in the vadose zone during and after major precipitation events in contaminated areas of Rocky Flats Plant, and (2) to study the chemical characteristics of actinides in interstitial waters held by the soil aggregates at various matric potentials (0 - 50 kPa). The water flow data obtained in-situ will be used to test the infiltration rates and flow estimates calculated by the various geohydrological models in use at RFP. Moreover, the water flux estimate is crucial measurement to assess solute flux down the soil column. The chemical characterization will include: (1) total concentrations of Pu and Am in soil interstitial waters that move freely (0-5 kPa) down the soil column, (2) fractionation of actinides in dissolved (< 0.1u) and particulate matter in freely flowing waters (0 - 5 kPa) and various matric potentials (5-10; 10 - 30; 30 - 50 kPa), (3) TOC, DOC, and pH, (4) major cations and anions, and (5) minor and trace elements that according to Phase I study exceeded the designated level. These data will be used to appraise the magnitude and physicochemical characteristics of actinide transport down the soil column.

SYSTEM DESCRIPTION

Soil Solution Sampler Apparatus

Zero-tension sampler

The zero-tension sampler will be made of 40-cm segments of polyvinyl chloride (PVC) tray (25 cm width) with one end plugged with a PVC stopper containing a collecting tube and the other end sharpened. The sharpened end will be driven into the pit face with a mallet to ensure minimal structure and textural disturbance to the soil. The water sampled by the zero-tension sampler will be collected by a bottle mounted on a load cell. The amount of water in the collection bottle and temperature will be simultaneously transmitted to a data logger. The transmitted information will be transferred daily to a receiving station via telemetry. The soil pits will be refilled after access tubes are placed to prevent convergence flow and to minimize further disturbance. The zero-tension soil solution samplers will be placed every 10 cm down the soil column to the depth of the caliche horizon or other semi-impermeable layer in 3-5 soil pits east of 903 Pad.

Fluxmeter

The fluxmeter consists of three components: (1) three tensiometers connected to differential pressure transducer, (2) a Teflon cylinder which is treated with silica to reduce hydrophobicity, and (3) a pump with a buffer container. Each fluxmeter will be installed with three soil moisture sensors at both sides and connected via Teflon tubing to a differential pressure transducer. The matric potential of the soil will be measured by the soil moisture sensor or tensiometer. Once the matric potential in the soil exceeds a pre-set value the pump will be activated to produce an equivalent vacuum inside the tension sampler.

Two fluxmeters will be installed in each pit excavated for the zero-tension sampler at two different depths. This approach will enable us to compare the mobility of actinides in various water pools within the soil environment.

The frequency, duration and intensity of summer precipitation will be determined by a rain gauge. This rain gauge is an integral part of the proposed apparatus and will be mounted east of 903 pad. The rain gauge will transfer the data simultaneously to the 21X data logger which will transmit this information via telemetry to a Base Station in T130B. The amount and nature of precipitation and soil water flux will be checked daily. The frequency of field sampling will be determined on the basis of the transmitted data.

The amount of water that can be collected by this apparatus in RF soils is currently unknown. One to two liters of interstitial waters were collected during snowmelt and after every major precipitation event in forested and alpine ecosystems (Litaor, in review).

Concluding Remark

The immense scope of PHASE II RFI/RIFS Work Plan for Operable Unit NO. 2 is obvious. The possible scientific gains from this work are incredible. Thus, I would like to assume the responsibility on the surficial soil program within this project. I shall report any plans, problems, progress, and findings directly to you and Pete Folger. My ultimate goal is to publish this work in a refereed journal. This approach will bring us the credibility and recognition by the community.

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